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Mediator-Template Assembly of Nanoparticles

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The ability to construct size- and shape-controllable architectures using nanoparticles as building blocks is essential for exploring the properties of nanostructures. Our mediator-template strategy explores multidentate ligands as molecular mediators and surfactant-capped nanoparticles as templates in order to build size-controllable and monodispersed particle assemblies. Such assemblies display both soft and hard properties, depending on how they interact with their substrates. This duality could form the basis of a new strategy for manipulating nanoscale linkages, soldering nanoelectronics, and constructing nanosensor devices. The assemblies also allow for controlled disassembly and size regulation by a third molecular component, which could lead to developments in nanotechnological applications in controlled drug delivery.

Many areas of nanotechnology involve the use of nanoparticle-based materials in applications such as sensors, catalysis, and information storage. These applications require the ability to assemble nanoparticles into a structure with controllable size, shape, and interparticle spatial properties, resulting in unique nanoscale properties that can be effectively exploited. While a variety of assembly methods have been demonstrated, the ability to precisely control size, shape, and interparticle spatial properties is rarely reported due to the lack of molecular-level understanding of the interparticle interactions and reactivities.

The key element of our assembly approach is a mediator-template strategy. The understanding of molecular driving forces exerted by molecular linkers or multidentate thioethers as mediators, as well as monolayer or surfactant capping molecules as templating agents, could lead to a general assembly strategy that would maximize our ability to control the structure's size, shape, and spatial properties. Consider, for example, a system in which multidentate thioethers, $Me_{4-n}Si(CH_2SMe)_n$ (**2**), are used as mediators and tetraalkylammonium bromides, $[CH_3(CH_2)_m]_4N^+Br^-$ (**1**), are used as templating agents. **Scheme 1** illustrates the general concept of the **2**-mediated assembly of **1**-capped gold nanoparticles (**1**/Au). This mediator-template combination is simple and effective. The mediation force exploits the coordination reactivity between **2** and Au, which can be manipulated by the number of thioether groups on **2**. Simultaneously, the templating force resulting from the surfactant reactivity of **1** determines the geometry of the assembly, depending on the chain length and structure of **1**.

(from left to right) Lisa Cousineau, Li Han, Mathew Maye, Lingyan Wang, Qiang Rendeng, Nancy Kariuki, Mark Schadt, Yan Lin, Jin Luo, Stephanie Lim, Kaylie Young, Chuan-Jian Zhong (Group leader), Elizabeth Crew, Derrick Mott, Peter Njoki, and Xiangting Dong.

The average diameters of the spherical assembly (the TEM image in Scheme 1) are dependent on the relative ratios of mediators vs. templates. One important finding is from a small-angle x-ray scattering measurement that (**Figure 1A**) [1] revealed a subtle decrease of the edge-to-edge distance with increasing mediator-to-template ratio, falling between the expected molecular lengths of **1** and **2**. Another important finding is from a spectrophotometric measurement of the surface plasmon resonance

band (**Figure 1B**) [2], which led to two important findings: that the mediator-template assembly of nanoparticles is an enthalpy-driven process, and that the enthalpy change (-1.3 kcal/mole) is close to the magnitude of the van der Waals interaction energy for alkyl chains. These findings establish the important role played by the templating molecules in the mediate-template assembly.

The spherical assembly on mica does not wet the surface, and thus retains its shape. In contrast, the spherical assembly wets highly ordered pyrolytic graphite (HOPG), and thus the particles tend to spread over the surface. The interaction between the spherical assembly and HOPG must be relatively strong in view of the hydrophobic character of the HOPG surface and the hydrophobic character of **1**-capped Au nanoparticles and their assemblies.

The soft-hard nature of the nanoparticle assemblies and their interactions with contacting substrates could form the basis of a new strategy for manipulating nanoscale linkages, soldering nanoelectronics, and constructing nanosensor devices. Interestingly, the nanoparticle assemblies display interesting optical properties that are highly responsive to changes in assembly size, chemical environment, and molecular structures. The chemically responsive optical properties could find applications in devices such as sensors and biosensors. Such assemblies also allow for controlled disassembly and size regulation by a third molecular component, which could form the basis of nanotechnological applications in controlled drug delivery.

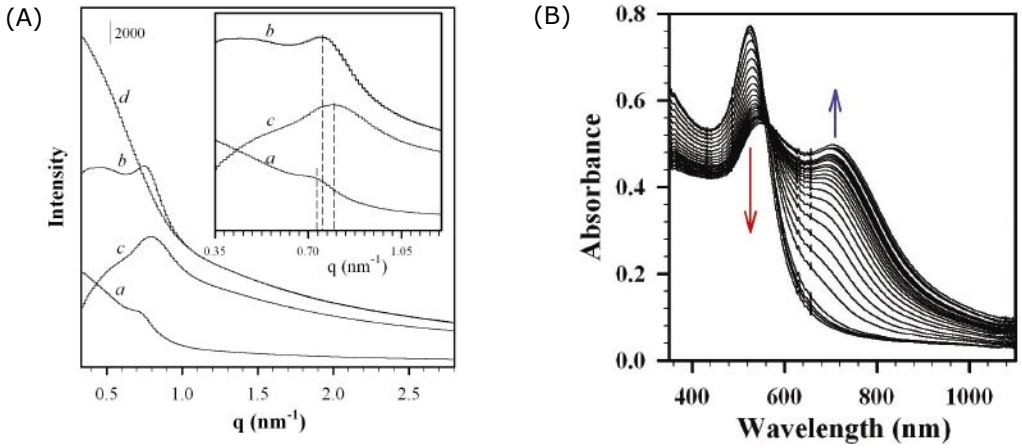
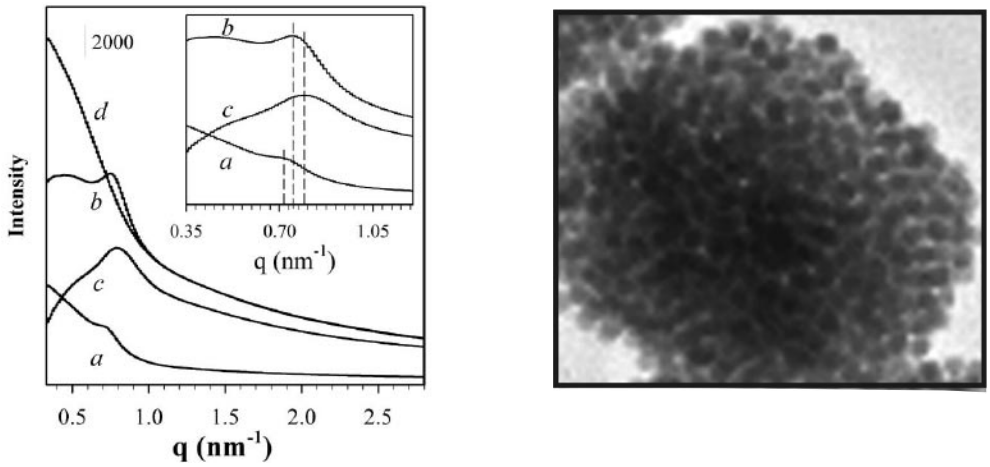


Figure 1. *(A) SAXS data for the* **2***-mediated assembly of* **1***/Au in solutions at three different concentration ratios (r = 2.5 (a), 10 (b), and 400 (c)). Curve d is for* **1***/Au solution. Inset: a magnified view of the peak region. (B) UV-Vis spectral evolution for the assembly of* Au_{nm} *upon addition of* **2** *(T = 5 °C). The spectral evolutions were recorded within the time frame of one hour.*



Scheme 1. *A schematic illustration of the mediation-template strategy for* **2***-mediated assembly of* **1***-capped gold nanoparticles. The right image shows an example of the assembly.*